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Dimerisation of Uranyl Nitrate Complexes in Trialkylphosphate Solutions

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Abstract

The molecular volumes of uranyl nitrate complexes have been determined from diffusion coefficients and viscosities by an approximate method using Stokes' law. The diffusion coefficients in trimethyl-, triethyl-, and trioctyl-phosphate and in a mixture of trioctyl phosphate/dodecane at 298 K were measured by use of an analytical ultracentrifuge as a function of the uranium concentration. The viscosity *B* coefficient and Stokes' radius were calculated for each system and compared with data obtained from tributyl phosphate solutions. It was confirmed by measurements of the partial molar volumes, that only in trimethyl phosphate solutions the structure of the complex is dimer or even tetramer.

Introduction

Stable complexes of uranyl nitrate are formed with phosphate esters and the formula $UO_2(NO_3)_2L_2$ was found by elemental analysis for different trialkyl phosphates (L: TMP = trimethyl phosphate, TEP = triethyl phosphate, TBP = tributyl phosphate, TOP = trioctyl phosphate) [1, 2]. The crystal and molecular structures of some uranyl nitrate complexes are already known, but only a few attempts have been made to gain an insight into the structure of these derivatives in solution [3, 4].

Organophosphorus compounds are widely used in commercial processes for selective solvent extraction of uranium. Due to this fact the knowledge of the structure and behaviour of the products in the organic phase is very important for modelling the operations performed, e.g. in the PUREX-Process. For these calculations detailed information about the transport phenomena has been needed, in order to simulate the extraction process of the relevant species.

In the present paper an analytical ultracentrifuge was used to determine the molecular parameters, including diffusion coefficients, particle size and interacting forces between solvent and solute. In a capillary-type cell an initially sharp boundary is obtained by shifting a solution over a more concentrated one, while the ultracentrifuge is in operation. The motion of the solute particles, caused by the chemical potential, leads to a spreading of the boundary. By means of light, transmitted through the rotating cell, the optical systems of the analytical ultracentrifuge translate particle movement into optical patterns. As a result, the diffusion coefficients were evaluated using both the Schlieren and UV-absorption optical systems.

The measurements were carried out at different uranium concentrations in order to extrapolate values obtained at finite concentration to those being valid at infinite dilution. Since the data in the TBP solutions gave straight lines, which were only slightly dependent on the concentration, only weak interactions were expected between the solvent and the solute [5]. Therefore the extrapolation to zero concentration of the solute can be performed easily, thus obtaining the D_0-value, depending only on the absolute temperature, T, of the system and the frictional coefficient, f, of the solute molecule in pure solvent:

$$D_0 = kT/f$$

According to Stokes' law the frictional coefficient is related to the radius, r, of a sphere, moving through a medium of viscosity, η [6]:

$$f = 6\pi\eta r$$

Therefore, the volume of the sphere can be derived from the diffusion coefficients and viscosity measurements. The application of this relation is based on the assumption that the uranium complexes are unsolvated particles in organic solutions. In order to prove this assumption, a series of uranium complexes were investigated, since the different lengths of the chains in the trialkyl phosphates are responsible for a significant change in the molecular weight and molecular volume.

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Furthermore, the measurement of the solution viscosity is another method to gain an insight into the properties of the complexes, since the well known viscosity B coefficient of the semi-empirical Jones–Dole equation depends not only on the transport behaviour but also on the structure of the solute molecules [7]:

$$\eta/\eta_0 = 1 + A\sqrt{c} + Bc$$

On the other hand, in these organic systems the partial molar volume calculated from density measurements provides reliable data for the molecular volume of the solute. The comparison of those values derived by different methods shows the dimerisation of the uranium complex in TMP solutions, whereas in the other systems investigated monomers are formed.

Experimental

The trialkyl phosphate complexes were prepared by extraction of uranyl nitrate from solid $UO_2(NO_3)_2\cdot6H_2O$, which was added in excess. The organic phase was separated from the water of crystallization and dried over a molecular sieve. For the pure solvents the drying procedure was tested by ^1H NMR spectroscopy [8]. In the presence of uranyl nitrate this drying procedure was even easier, since the water was displaced by the more stable uranyl nitrate complex and therefore expelled out of the organic phase. The uranium concentration in the organic solutions was titrated using standard EDTA solution [9]. For the saturated solutions the ratio of trialkyl phosphate to uranyl nitrate, which has been reported to be 2:1 in the complex, was verified.

Since all dilute solutions were prepared gravimetrically by weighing definite quantities of stock solutions, concentrations could be determined precisely by density measurements. These were carried out by a digital densitometer, which was accurate to within the 4th decimal place, air and twice-distilled water being used for calibration. This procedure was checked by comparing the data of the pure solvents with values found in the literature [10]. The organic solutions were stored in the dark in order to avoid photoreduction.

The Beckman Instruments Ltd. Model E Analytical Ultracentrifuge has become a standard tool for the study of diffusion, although the assembling of the cell and the operation of the Model E are troublesome and time-consuming. All measurements were carried out at 25.00 °C using a capillary-type centerpiece consisting of two compartments which could be filled separately. For the diffusion measurements one sector was filled with 0.12 ml of the organic solution, the other sector with 0.36 ml of the organic solvent. The cell was fitted into a titanium rotor and accelerated to a final measurement velocity of 5.200 rpm. Under centrifugal force, the solvent began to drain through the capillary into the solute sector, creating a sharp boundary by overlaying the test solution there.

The cell assembly was constructed in a manner which permitted light rays to pass through. The Schlieren optical system was used for analysing the refractive index gradient, thus providing a plot of the concentration gradient at the boundary, since a change in the refractive index is proportional to a change in concentration. The Schlieren photos were transmitted by an electronic camera to a bit-plane processor, where the values of the height and the area of the Schlieren-peak were evaluated by a pattern-considering system (PACOS) and stored in a command-protocol dataset [11]. By means of the absorption optical system the concentration profiles of the uranyl nitrate complex were obtained, measuring the absorption at 425 nm *versus* the distance from the axis of rotation. The diffusion coefficients were calculated in the usual way from the change of the optical patterns recorded at preselected intervals during the run [12]. The results obtained with both optical systems were in agreement with each other, the error limit being ±3%.

Viscosities were measured on a Schott Ltd. 'AVS' instrument using a calibrated Ubbelohde-type viscometer. The values of the viscosity η were calculated from the flow-times and densities (Tables I and II).

Results and Discussion

When measuring the diffusion coefficients by use of the analytical ultracentrifuge, the centrifugal force supports the formation of a sharp boundary at the beginning of the experiment. The movement of the particles of interest from the higher concentrated solution to the dilute solution was not influenced by sedimentation effects, since a low rotor speed was used. From the concentration profiles the differential diffusion coefficients, D, were determined at a concentration, c, which was constant in the middle of the boundary. This concentration c was calculated from $(c_1 + c_0)/2$, where c_1 and c_0 mean the concentration of the complex in the solution and in the solvent or a more diluted solution, respectively. The mean values of the diffusion coefficients obtained with both the Schlieren and the absorption optical system are given in Table III.

The results show that the diffusion coefficients depended linearly on the concentration of the organic complex or even were independent of it. Similar behaviour to the systems investigated within this work was found on comparison with that of the uranyl nitrate complex in the TBP systems [4]. In the usual derivations of the expressions used for the calculation of molecular parameters, it was implicitly

TABLE I. Viscosity and Density of $UO_2(NO_3)_2 \cdot 2TEP$

$c \times 10^2$ (g cm^{-3})	1.517	3.034	4.551	6.068	7.585	11.377
ρ (g cm^{-3})	1.0702	1.0762	1.0825	1.0885	1.0945	1.1097
η (cP)	1.582	1.618	1.658	1.694	1.729	1.828
η_{sp}/c (g^{-1} cm^3)	1.57	1.56	1.61	1.58	1.57	1.61

TABLE II. Viscosity Coefficients (*B*) and Density Coefficients (*m*) of $UO_2(NO_3)_2L_2$ in Different Solvents and Viscosities and Densities of the Solvents

Solvent	ρ (g cm^{-3})	η (cP)	*B* (cm^3 g^{-1})	*m*
TMP	1.2095	2.010	1.78	0.4164
TEP	1.0641	1.545	1.57	0.4007
TOP	0.9210	11.667		0.2569
30/70 TOP/n-dodecane	0.7973	2.120	1.18	0.2537

TABLE III. Diffusion Coefficients (*D*) of $UO_2(NO_3)_2L_2$ in Different Solvents

In TMP						
c (M)	0.01	0.02	0.04	0.06	0.08	0.10
$D \times 10^6$ (cm^2 s^{-1})	1.43	1.41	1.48	1.44	1.43	1.46
In TEP						
c (M)	0.01	0.02	0.04	0.06	0.08	0.13
$D \times 10^6$ (cm^2 s^{-1})	2.77	2.76	2.98	2.99	3.00	2.89
In TOP						
c (M)	0.01	0.02	0.04	0.06	0.08	0.13
$D \times 10^6$ (cm^2 s^{-1})	0.27	0.28	0.27	0.29	0.28	0.30
In 30/70 TOP/n-dodecane						
c (M)	0.01	0.02	0.04	0.06	0.07	0.08
$D \times 10^6$ (cm^2 s^{-1})	1.43	1.39	1.48	1.51	1.57	1.57

assumed that the laws of dilute solutions are obeyed. Since the concentration has no significant influence on the diffusion coefficients, interactions of the solute molecules with each other and with the solvent molecules, which would lead to a marked concentration dependence, can be excluded.

The values of the diffusion coefficients D_0 extrapolated to infinite dilution are to be seen in Table IV. The physical behaviour and the chemical properties of the organic solutions are considered to depend dominantly on a molecular kinetic point of view of the characteristics of individual solute molecules. Therefore it is assumed that the diffusion measurements will provide a kind of submicroscopic picture of the structure in the solutions by use of the kinetic laws. The size of the complex molecule, depending on the molecular weight, has been related to the diffusion coefficient by Stokes' radius, *r*. For experiments performed at the same temperature *T*, the values of the diffusion coefficients in different solvent systems are commonly compared, taking the solvent viscosity, η_0, into consideration, since it has been related to the frictional coefficient of the solute. As can be seen from Table II the viscosities of the trialkyl phosphates vary by a factor of 10. The values of the diffusion coefficients, therefore, will decrease by the same order of magnitude if the solvent viscosity becomes higher. The validity of the equation has been discussed in detail for several different systems and Stokes' law has often been used to describe diffusion of molecules having dimensions comparable to those of the solvent molecules [13]:

$$D = \frac{RT}{6\pi\eta r N_A}$$

The radii of the organic complexes, calculated by use of the universal gas constant *R* and Avogadro's constant N_A are given in Table IV. A systematic increase of the values *r* will be seen, if the chain length of the complexing agent is extended in the series TEP to TOP. For the TMP system, the radius is larger than for TEP, indicating that there is a larger unit of the complex present in the solution. The different values of the uranyl nitrate complex in those systems, to which dodecane was added for dilution, may be explained by a change of the structure of the solvent, since a marked volume extension becomes obvious whenever TBP is mixed with dodecane. In the TOP/n-dodecane mixture, however, no change in volume could be detected when the two solvents were put together.

TABLE IV. Diffusion Coefficients (D_0), Radii (*r*) and Volumes (*V*) of $UO_2(NO_3)_2L_2$ in Different Solvents

Solvent	$D_0 \times 10^6$ (cm^2 s^{-1})	*r* (nm)	V_1 [b] (nm^3)	V_2 [b] (nm^3)
TMP	1.44	0.754	1.80	0.54
TEP	2.78	0.516	0.58	0.71
TBP[a]	1.10	0.596	0.89	1.05
30/70 TBP/n-dodecane[a]	2.60	0.533	0.63	1.02
TOP	0.27	0.693	1.39	1.69
30/70 TOP/n-dodecane	1.43	0.720	1.56	1.70

[a] Data from ref. 4. [b] Volumes are from V_1 = diffusion, V_2 = density measurements.

Since the volume of a sphere equals $\frac{4}{3}\pi r^3$, the volume, V_1, was calculated from the Stokes' radius of each organic complex. The values V_1, given in Table IV, should correspond to the volume of the solute particle. A precise value for the volume of the particles cannot be expected by this procedure, since it is limited by the fact that the molecules are not ideal spheres, therefore causing deviations from Stokes' law. Although the experiments were performed at low rotor speeds, for the lower values in the organic systems the effect of pressure must be taken into account. In order to confirm the information gained by this method, the volumes should be compared with data which were derived by another analytical procedure, e.g. as density measurements or by crystal diffractometry, on condition that the structure in the solid phase can be compared with that in solution.

The density and viscosity measurements were carried out for each system in order to characterize the solutions under investigation. When uranyl nitrate is added to the organic solutions there is a linear increase of the density and the specific viscosity of the solution which depends on the complex concentration. The relevant data for the uranyl nitrate·2TEP-complex are given in Table I. Since similar behaviour is observed for all the trialkyl phosphates, the characterization of those systems can be summarized by a linear function for the density and viscosity, respectively.

The viscosity B coefficients, calculated from the Jones–Dole equation are given in Table II. By use of these B values the viscosity of any solution can be derived approximately, since the A coefficient is quite near to zero and may be neglected. The positive B coefficients indicate that the behaviour of uranyl nitrate in solution can be described as a 'structure maker' [14]. This influence is very strong in the TMP system, whereas it will decrease if the chain length of the trialkyl phosphate becomes longer. Interpretation of the B values will not give the effective volume of the solute molecules, since a change in the shape factor has to be considered for the different solvent systems. If this factor is not exactly known, the calculation will lead to erroneous results.

If the density of the solution, ρ_3, is plotted against the concentration, c_2, of the complex, the density coefficient, m, can be obtained from the slope. The density of the pure solvent mixture, ρ_1, equals the data obtained at zero concentration:

$$\rho_3 = \rho_1 + (1 - V^*\rho_0)c$$

The slope m stands for $1 - V^*\rho_0$, where V^* is the partial specific volume of the complex and ρ_0 is the density of the complexing agent. In the TOP/n-dodecane mixture ρ_0 is the density of pure TOP, since the n-dodecane is added as an inert solvent for dilution. For the trialkyl phosphate solutions without n-dodecane, no difference in the solvent densities has to be considered, that means $\rho_1 = \rho_0$. In the TMP and TEP systems any dilution with n-dodecane at a 30/70 ratio is impossible, because the mixture splits into two phases. By means of the solvent density, ρ_1, and the slope m given in Table II, the density ρ_3 of any solution can be calculated up to very high uranium concentrations. This behaviour shows that there are only slight changes in the volume of the particles when the complex is formed. The values of the density coefficient m will show a systematic decrease, if the chain length of the trialkyl phosphates is increased. The density of the complex, $\rho_2 = 1/V^*$, decreases in a similar way, since the density of the complexing agent becomes less. The densities of the uranyl nitrate complex with TMP ($\rho_2 = 2.0725$ g cm^{-3}) and with TEP ($\rho_2 = 1.7756$ g cm^{-3}) are slightly smaller than the data calculated from the crystal structure [1, 2].

The volume of a single molecule V_2 can be derived from the partial specific volume, V^*:

$$V_2 = MV^*/N_A$$

For this calculation the molecular weight M of the complex must implicitly be known. Therefore by this method alone it is impossible to distinguish whether dimers of the complexes are formed in the solutions or not. In the case of the TMP system the volume of the complex molecule may be 0.54 nm^3 for $UO_2(NO_3)_2 \cdot 2TMP$ or 1.08 nm^3 for $(UO_2(NO_3)_2 \cdot 2TMP)_2$. The value for the dimer is in agreement with that for the unit cell of the crystal (1.0221 nm^3) containing two molecules. The values V_2 given in Table II for the different trialkyl phosphate complexes will correspond to the values V_1 obtained from the diffusion measurements, if the uranyl nitrate complex with TMP is considered to be a tetramer and the other complexes to be monomers only.

The dependence of the molar volume MV^* on the molecular weight M can be seen from Fig. 1. If the molar volumes of the pure solvents are plotted against the molecular weight of the solvents, a linear relation will be obtained:

$$M_L V^*_L = a_L M_L + b_L$$

In this equation, L, stands for the trialkyl phosphates and the coefficients found empirically are $a_L = 1.203$ cm^3 g^{-1} and $b_L = -49.7$ cm^3 mol^{-1}. For the uranyl nitrate complexes a similar straight line is obtained with the coefficients $a_C = 1.177$ cm^3 g^{-1} and $b_C = -465.3$ cm^3 mol^{-1}, respectively, where C stands for the complex. Since both lines have nearly the same slope, the theoretical molar volume of uranyl nitrate $M_U \cdot V^*_U$ in the complexes with two organic ligands may be derived by subtracting twice the molar volume of the solvent from the molar volume of the complex.

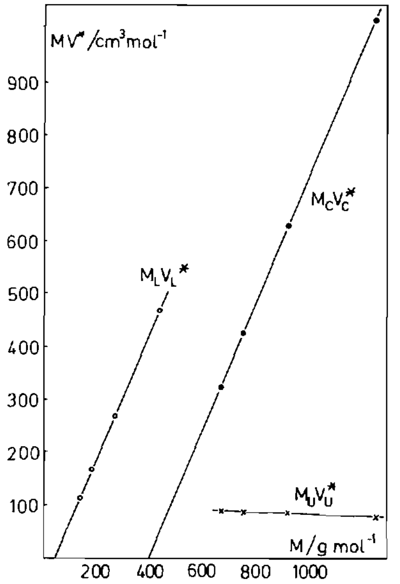

Fig. 1. Dependence of molar volumes of the solvents, the complexes and uranyl nitrate on the molecular weights.

$$M_U V^*_U = a_C M_C - 2a_L M_L + b_C - 2b_L$$

As can be seen from Fig. 1, the function resulting from that subtraction again shows a straight line. The theoretical volume of uranyl nitrate in each of the complexes can be calculated, e.g. in the TBP system the molar volume will be 84 cm^3 mol^{-1}, corresponding to a density of 4.69 g cm^{-3}, if the volume of TBP is considered to be constant. The decreasing values of the theoretical volume of the uranyl nitrate with increasing molecular weight of the organophosphorus compound shows, however, that there are some interactions when the complexes are formed. On the other hand, the functions may be used to calculate the molecular parameters of trialkyl phosphates of similar structure, which have not been investigated in this work. In order to prove the validity of this method the investigations have to be continued in systems where the solute molecules are small.

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